

PATENT SPECIFICATION

(11) 1 423 403

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- (21) Application No. 4962/73 (22) Filed 31 Jan. 1973
 (31) Convention Application No. 11505/72 (32) Filed 1 Feb. 1972 in (19)
 (33) Japan (JA)
 (44) Complete Specification published 4 Feb. 1976
 (51) INT CL² B05D 5/12
 (52) Index at acceptance

B2E 180 18Y 209 233 236 23Y 240 246 273 29X 30X 32X
 32Y 33X 380 382 383 384 385 386 387 38X 38Y
 390 391 39X 39Y 410 413 416 41X 41Y 44Y 450
 452 453 454 455 456 469 479 483 495 496 497 498
 49Y 505 506 507 50X 50Y 515 516 52Y 531 555 55Y
 565 566 567 56Y



(54) COATED PLASTICS FILM FOR USE IN ELECTRO- PHOTOGRAPHIC COPYING

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coated plastics films for use for forming a toner image in an electrophotographic copying machines, and to a process of forming images on such sheets.

It is well known to carry out xerography in a commercial automatic copying machine, by forming a toner image on an electrically insulating photosensitive plate, and transferring this image to one or more sheets of paper or plastics film, fixing the image on the sheet, e.g. by heating to fuse the toner powder to the sheet, and passing the image-bearing sheet(s) out of the machine. As such sheets, it is customary to use polyester films

which is coated on at least one of its surfaces with a layer comprising

(a) a film-forming polymer selected from a poly(alkylacrylate), poly(alkylmethacrylate) or a mixture of (i) a copolymer of styrene and an alkylacrylate or alkylmethacrylate and up to 95% by weight of the mixture of (ii) nitrocellulose, a cellulose ester, a polymer formed by esterifying and polycondensing mixtures of acids including terephthalic acid, a polycarbonate, a polysulphone, polyvinylidene chloride or polyphenylene oxide, and

(b) 0.1 to 5% by weight, based on the weight of the polymer, of one or more matting agent,

the components (a) and (b) being selected such that the coated layer has a surface resistivity of 1×10^8 to 1×10^{15} ohm.

The thermal stability

ERRATA

SPECIFICATION No. 1,423,403

Page 2, line 42, *delete polysulphonates insert polysulphone;*

Page 2, line 121, *for had read has*

Page 4, line 59, *delete polysulphonate insert polysulphone*

THE PATENT OFFICE
30th March, 1976

... as defined below or at least 100°C containing more than 15% by weight of acrylo-

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It is well known to carry out xerography in a commercial automatic copying machine, by forming a toner image on an electrically insulating photosensitive plate, and transferring this image to one or more sheets of paper or plastics film, fixing the image on the sheet, e.g. by heating to fuse the toner powder to the sheet, and passing the image-bearing sheet(s) out of the machine. As such sheets, it is customary to use polyester films, which may be coated with an ester resin which is soluble in organic solvent.

These conventional coated films, however, have some drawbacks in that they give a coated image thereon of low optical density due to a low degree of thermal fixing, they tend to become electrostatically charged and therefore to attract dust; and when a pile of leaves of such a film is placed in a copying machine for the purpose of making multiple copies, two or more leaves are occasionally withdrawn at a time from the feeding tray due to adherence between the leaves (this is known as multiple feeding).

The objects of the present invention are to provide an electrophotographic film in which these defects are alleviated.

According to the present invention, there is provided a coated film for use in electrophotographic copying which comprises a plastics film having a thermal resistance temperature as defined below of at least 100°C

which is coated on at least one of its surfaces with a layer comprising

(a) a film-forming polymer selected from a poly(alkylacrylate), poly(alkylmethacrylate) or a mixture of (i) a copolymer of styrene and an alkylacrylate or alkylmethacrylate and up to 95% by weight of the mixture of (ii) nitrocellulose, a cellulose ester, a polymer formed by esterifying and polycondensing mixtures of acids including terephthalic acid, a polycarbonate, a polysulphone, polyvinylidene chloride or polyphenylene oxide, and

(b) 0.1 to 5% by weight, based on the weight of the polymer, of one or more matting agent,

the components (a) and (b) being selected such that the coated layer has a surface resistivity of 1×10^8 to 1×10^{15} ohm.

The thermal resistance temperature is determined according to ASTM test number D759—66 by measuring the softening point of the heated plastics films; see *Modern Plastics Encyclopedia*, 1971—1972, published by McGraw-Hill, Inc., pp. 622—625.

The electrophotographic film of the present invention has the advantage that it is superior to uncoated plastics films in adhesion of electrophotographic toner thereto because of the good adhesion obtained between the resin coating and the toner.

Suitable materials for use as the matting agent are powdered inorganic solids, such as silica or alumina, powdered starch or powdered plastics materials, such as polyethylene, polypropylene, poly(ethylene terephthalate), polystyrene, polycarbonates, acrylic esters, methacrylic esters, such as the alkyl acrylates or alkyl methacrylates having from 1 to 5 carbon atoms in the alkyl group, polyacrylonitrile or acrylonitrile copolymers such as those containing more than 15% by weight of acrylo-

SEE ERRATA SLIP ATTACHED

nitrile (e.g., acrylonitrile-acrylic acid ester, acrylonitrile-methacrylic acid ester, acrylonitrile - vinyl acetate, acrylonitrile - vinyl chloride, acrylonitrile - acrylamide, acrylonitrile-styrene, acrylonitrile - butadiene and acrylonitrile - styrene - butadiene). Mixtures thereof can also be used. Plastics matting agents used will generally have a molecular weight of from 10,000 to 200,000, more preferably from 50,000 to 150,000.

It is preferred to employ a matting agent or agents having a particle size of from 0.01 to 20 microns. When the particle size is smaller than 0.01 micron, two or more leaves of the film will often be withdrawn together from a feeding tray; on the other hand, a particle size greater than 20 microns results in a rough-surfaced opaque film.

The matting agent is incorporated in an amount of 0.1 to 5%, more desirably 0.5 to 3%, by weight based on the weight of the film-forming polymer. An amount of matting agent of less than 0.1% by weight does not achieve the objects of the present invention, i.e., there will occur multiple feeding of two or more leaves of the film from a feeding tray, and an amount of over 5% by weight results in a rough-surfaced opaque film.

The film-forming polymer used in the coated layer preferably has a molecular weight of from 10,000 to 200,000.

When a styrene copolymer is used as the film-forming polymer, it is admixed with up to 95% by weight (of the total resins present in the coating) of another resin as specified above in order to increase its thermal resistance. Examples of these other resins are cellulose acetate and other cellulose esters which are soluble in organic solvents, polymeric terephthalic acid mixed esters as disclosed in U.S. Patent No. 3,100,722, polycarbonates, polysulphonates, polyvinylidene chloride and polyphenylene oxides having a molecular weight of from 100,000 to 250,000. The expression "polymeric terephthalic acid mixed esters" is meant to designate known co-polyesters which are obtained by esterification and polycondensation of mixtures of acids containing terephthalic acid and at least one further dicarboxylic acid, e.g. isophthalic acid, ortho-phthalic acid, adipic acid or sebacic acid, with bifunctional alcohols containing up to 10 carbon atoms in the molecule, e.g., ethylene glycol, trimethyleneglycol, tetramethyleneglycol, pentamethyleneglycol, hexamethyleneglycol, heptamethyleneglycol, decamethyleneglycol and propyleneglycol; excellent results are obtained when using mixed esters obtained from mixtures of acids containing per 100 mols of terephthalic acid 10 to 50 mols of said other dicarboxylic acid.

The coated films in accordance with the present invention can be prepared as follows:—

A solution of the resin is prepared in a

solvent such as an alcohol, for example, methanol and ethanol; a ketone, for example, acetone and methyl ethyl ketone; or a chlorinated hydrocarbon, for example, methylene chloride, ethylene chloride and tetrachloroethane; or a mixture thereof.

A matting agent and, optionally, a pigment, an antistatic agent and other known additives is/are added, with stirring, to a solution of resin and the resulting mixture is then filtered to produce a coating solution. This solution is then applied to one or both sides of a thermally resistant (as defined above) plastics film (e.g., made of a polyester, polysulphone, poly(phenylene oxide), polyimide, polycarbonate, cellulose ester or polyamide), which retains sufficient mechanical strength for use in a dry xerographic machine at temperatures above 100°C. Plastics films having lower thermal resistance are unsuitable because they are wrinkled, curled or otherwise deformed when thus used. The film is preferably 50 to 200 microns in thickness.

The coated layer preferably has a dry thickness of 0.3 to 10 microns. A coated layer having a thickness of less than 0.3 micron causes interference stripes, and a layer having a thickness of greater than 10 microns causes excessive curing of the film after thermal fixing.

The surface resistivity of the coating must be within the range of from 1×10^9 ohm to 1×10^{15} ohm. A surface resistivity below 1×10^9 ohm results in low image optical density, while a surface resistivity over 1×10^{15} ohm causes electrostatic pick-up of dust by the film during handling.

The electrophotographic film thus obtained fuses well with a toner to provide an image of a high optical density when employed for copying in an electrocopying machine, can be withdrawn from a stack in a feeding tray without multiple feeding, and has a minimal tendency to electrostatic pick-up of dust during handling thereof. The electrophotographic film of the present invention is also very suitable for use in two-sided copying and in an overhead projection system; known matt plastics films are unsuitable for use as an overhead electrophotographic projection film because of their opacity due to a high concentration of matting agent.

When only one surface of the thermally resistant plastics film is coated with the layer of resin and matting agent, the opposite surface is preferably coated with an antistatic coating layer, which generally had a dried thickness of less than 1.0 micron, preferably from 0.1 micron to 0.5 micron. The antistatic coating solution usually contains from 0.01% to 2.0% by weight of the antistatic agent. The solvent for the antistatic coating solution is usually the same as that which is used to dissolve the resin.

Further, from 0.5% to 5.0% by weight of a polymer may be dissolved as a binder in the antistatic coating solution having from 0.01% to 2.0% by weight of antistatic agent. In this case, the coated layer usually has a dried thickness of 0.5 micron to 3.0 micron. An antistatic coating solution containing a binder provides the same effect as an antistatic coating solution without binder but the antistatic effect provided is more durable, i.e., the antistatic layer contains 2.0% to 40.0% by weight of the antistatic agent based on the total weight of the binder resins.

Antistatic agents which may thus be used in the present invention are naphthalene sulphonates; ethylene oxide addition products; phosphoric esters; anionic surface active agents, such as alkyl metal sulphates, alkyl aryl metal sulphates, alkyl naphthalene metal sulphates or alkyl metal sulphonates, each having 10 to 20 carbon atoms in the alkyl group and the metal being sodium, potassium magnesium or calcium; and alkyl amine salts having 10 to 20 carbon atoms in the alkyl group with a metal such as sodium, potassium, magnesium or calcium, cationic surface active agents, such as alkyl dimethyl ammonium chlorides having 10—20 carbon atoms in the alkyl group, or dialkyl dimethyl ammonium chlorides having 10 to 20 carbon atoms in the alkyl group; and nonionic surface active agents, such as polyoxyethylene alkyl phenols having 10 to 20 carbon atoms in the alkyl group, and polyoxyethylenepolyalcohols, the alcohols being aliphatic alcohols having 10 to 20 carbon atoms.

Binder resins which can be used with antistatic agents in the antistatic layer are polyester resins, polyalkylacrylate resins, polyalkylmethacrylate resins, styrene-alkylacrylate copolymers, styrene-alkylmethacrylate copolymers, cellulose esters, polycarbonates, polysulphones, polyvinylidene chlorides or polyphenylene oxides.

According to a second aspect of the present invention, a method of electrophotography comprises

- (i) forming a toner image on an electrically insulating photosensitive surface and
- (ii) transferring this toner image to a coated plastics film of the first aspect of the invention.

The toner image can then be fixed onto the surface of the film, e.g. by heating.

The present invention will now be illustrated in more detail by the following examples, in which all parts and percentages are by weight. In both the examples, the copying films used were evaluated in an automatic xerographic copying machine marketed as the "Xerox 720" ("Xerox" is a registered Trade

Mark) by the Fuji-Xerox Co., in which a toner image is made and transferred by the aforesaid process, namely a selenium-coated electrophotosensitive plate is uniformly charged and dusted with toner powder, imagewise exposed to light, surplus toner powder is removed, some of the toner remaining on the plate is transferred to a copying sheet which is fed from a stack in a feeding tray, the sheet is heated to fuse the toner onto the sheet, the image-bearing sheet is discharged to a receiving tray and further sheets are fed to the image-bearing plate so as to form further copies.

Surface resistivity values were determined by interposing a test piece between a pair of 10 cm long brass electrodes spaced 0.14 cm from each other and reading the resistance value between the electrodes after 1 minute from switching on by means of an insulation tester. The surface of the electrode in contact with the test piece was plated with stainless steel. The test piece was subjected to the surface resistivity reading after conditioning at 23°C and 65% RH for about half a day.

EXAMPLE 1.

6 Parts of a copolymer of 20 mole% of styrene and 80 mole% of *n*-butyl methacrylate (of average molecular weight 120,000) were dissolved in 100 parts of a 2:2:1 mixture of acetone:methyl ethyl ketone:methylene chloride. 0.08 Part of sodium dodecylphosphate was added as an antistatic agent and 0.15 part of finely divided silicon dioxide (average particle size: 0.5 microns) was dispersed in the mixture as a matting agent. The resulting mixture was then filtered to remove any dust and obtain a coating solution. The coating solution was applied to a 100-micron thick polycarbonate film to form a coating layer of a surface resistivity of 6×10^{11} ohm, the coating layer having a dried thickness of 1.5 micron. To the reverse side of the film there was applied a solution of 1 part of antistatic agent, alkylbenzimidazole-sulphonate, in 500 parts of a 1:1 mixture of methanol:acetone to form a coating layer having a dried thickness of 0.5 micron.

In the following Table, the properties of the film are summarized and compared with those of the uncoated polycarbonate film, using the standards defined as follows.

Multiple feeding: Number of leaves withdrawn two or more at a time/Total number of leaves withdrawn from the tray.

The image density was evaluated by sight, and the adhesion of the toner by scratching the surface with a finger-nail. These properties were then evaluated in four grades from A (excellent) to D (poor).

| | Uncoated film | Coated film |
|-------------------|---------------|-------------|
| Image density | B | A |
| Multiple feeding | 25/25 | 0/25 |
| Adhesion to toner | D | A |

EXAMPLE 2.

1.5 parts of a copolymer of 65 mole% styrene with 35 mole% butylacrylate (average molecular weight: 80,000) 3.5 parts of an ester resin (marked as Ester-Resin 20 by Toyobo Co., Ltd. Japan) and 0.04 part of sodium dioctylphosphate as an antistatic agent were dissolved in 100 parts of a 18:1:1 mixture of methylene chloride:phenol:tetrachloroethane and 0.08 part of powdered polyacrylonitrile (average molecular weight: 200,000; average particle size: 1.0 micron) as a matting agent was dispersed on the solution. The resulting mixture was filtered to

remove dirt to obtain a coating solution. The coating solution was applied to both sides of a 100 micron thick polyester film to produce an electrophotographic film of a surface resistivity of 4×10^{12} ohm, the coating layers having a dried thickness of 2.0 micron.

The properties of the electrophotographic film thus obtained are summarized in the following Table where they are also compared with those of an ester resin (Ester-Resin 20) coated polyester film (Control 1) and of an uncoated polyester film (Control 2), using the same standards as in Example 1.

| | Control 1 | Control 2 | Coated film |
|-------------------|-----------|-----------|-------------|
| Image density | B | B | A |
| Multiple feeding | 25/25 | 25/25 | 0/25 |
| Adhesion to toner | A | D | A |

It will be seen from the Examples that the films of the invention are superior to the uncoated films and to films coated with esters in known manner.

Our prior application No. 844/73 (Serial No. 1,413,201) claims a method of electrophotography of the type described and claimed herein, using a plastics film of the type claimed herein but wherein the polymer is only of styrene and an acrylic or methacrylic ester and the surface resistivity of the coated layer is not referred to.

WHAT WE CLAIM IS:—

1. A coated film for electrophotography, which comprises a plastics film having a thermal resistance temperature (as hereinbefore defined) of at least 100°C which is coated on one or both of its surfaces with a layer comprising

(a) a film-forming polymer selected from a poly(alkylacrylate), poly(alkylmethacrylate) or a mixture of (i) a copolymer of styrene and an alkylacrylate or alkylmethacrylate and up to 95% by weight of the mixture of (ii) nitrocellulose, a cellulose ester, a polymer formed by esterifying and polycondensing mixtures

of acids including terephthalic acid, a polycarbonate, a polysulphonate, polyvinylidene chloride or polyphenylene oxide, and

(b) 0.1 to 5% by weight, based on the weight of the polymer, of one or more matting agent,

the components (a) and (b) being selected such that the coated layer has a surface resistivity of 1×10^9 to 1×10^{15} ohm.

2. A film as claimed in Claim 1, wherein the polymer has a molecular weight of from 10,000 to 200,000.

3. A film as claimed in any preceding claim, wherein the matting agent is selected from powdered inorganic solids, starch and powdered plastics materials.

4. A film as claimed in Claim 3, wherein the powdered plastics material is polyethylene, polypropylene, poly(ethylene terephthalate) polystyrene, a polycarbonate, a polyacrylic ester, a polymethacrylic ester, polyacrylonitrile, acrylonitrile copolymer or a mixture thereof.

5. A film as claimed in Claim 3 or 4, wherein the powdered plastics material has a molecular weight of from 10,000 to 200,000.

6. A film as claimed in Claim 3, wherein

the powdered inorganic solid is silica or alumina.

7. A film as claimed in any preceding claim, wherein the matting agent has a particle size of from 0.01 to 20 microns.

8. A film as claimed in any preceding claim, wherein the plastics film has a thickness of 50 to 200 microns, and is made of a polyester, polysulphone, poly(phenylene oxide), polyimide, polycarbonate, cellulose ester or polyamide.

9. A film as claimed in any preceding claim, wherein the or both coating layers has or have a dried thickness of 0.3 to 10 microns.

10. A film as claimed in any of Claims 1 to 8, wherein the plastics film is coated on one surface with a coating layer as claimed in any preceding claim, the other surface being coated with an antistatic layer containing an antistatic agent.

11. A film as claimed in Claim 10, wherein the antistatic agent is selected from naphthalene-sulphonates, ethylene oxide addition products, phosphoric esters, anionic surface active agents, cationic surface active agents and nonionic surface active agents.

12. A film as claimed in Claim 11, wherein the anionic surface active agents are alkyl metal sulphates, alkyl aryl metal sulphates, alkyl naphthalene metal sulphates or alkyl metal sulphonates, each having 10 to 20 carbon atoms in the alkyl group and the metal being sodium, potassium, magnesium or calcium or alkyl amine salts having 10 to 20 carbon atoms in the alkyl group and the metal being sodium, potassium, magnesium or calcium.

13. A film as claimed in Claim 11, wherein the cationic surface active agents are alkyl dimethyl ammonium chlorides or dialkyl dimethyl ammonium chlorides, both having 10 to 20 carbon atoms in the alkyl group.

14. A film as claimed in Claim 11, wherein the nonionic surface active agents are polyoxyethylene alkyl phenols, having 10 to 20 carbon atoms in the alkyl group, or polyoxyethylene-polyalcohols, the alcohols being aliphatic alcohols having 10 to 20 carbon atoms.

15. A film as claimed in any of Claims 10 to 14, wherein the antistatic layer contains from 0.01% to 2.0% by weight of the antistatic agent.

16. A film as claimed in any of Claims 10

to 15, wherein the antistatic layer has a dried thickness of 0.1 to 0.5 microns.

17. A film as claimed in any of Claims 10 to 15, wherein the antistatic layer contains from 0.5% to 5.0% by weight of a binder resin.

18. A film as claimed in Claim 17, wherein the binder resin is selected from polyester resins, polyalkylacrylate resins, polyalkylmethacrylate resins, styrene-alkylacrylate copolymers, styrene-alkylmethacrylate copolymers, cellulose esters, polycarbonates, polysulphonates, polyvinylidene chlorides and polyphenylene oxides.

19. A film as claimed in Claim 17 or 18, wherein the antistatic layer contains 2.0% to 40.0% by weight of antistatic agent based on the total weight of the binder resin.

20. A film as claimed in Claim 17, 18 or 19, wherein the antistatic layer has a dried thickness of 0.5 to 3.0 micron.

21. A film as claimed in Claim 1, substantially as herein described with reference to any of the Examples, apart from comparative samples.

22. A method of electrophotography which comprises

(i) forming a toner image on an electrically insulating sensitive surface and

(ii) transferring this toner image to a coated plastics film as claimed in any preceding claim.

23. A method as claimed in Claim 22, substantially as hereinbefore described with reference to any of the foregoing Examples, apart from comparative samples.

24. A method as claimed in Claim 22 or 23, wherein the toner image is subsequently fixed by heating to fuse the toner.

25. A sheet of coated plastics film bearing a transferred toner image made by the method of any of Claims 22 to 24.

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